

CHAPTER 12

Modeling Chlorine Decay and the Formation of Disinfection By-Products (DBPs) in Drinking Water¹

Introduction

A major objective of drinking water treatment is to provide microbiologically safe drinking water. The combination of conventional drinking water treatment and disinfection has proved to be one of the major public health advances in modern times.

In the U.S., chlorine is most often the final disinfectant added to treated water for microbiological protection before it is discharged into a drinking water distribution system. However, disinfectants, especially chlorine, react with natural organic matter (NOM) to form disinfection by-products (DBPs), which are considered to be of concern from a chronic exposure point of view.

Drinking water disinfection, therefore, poses the dilemma of a risk tradeoff. Chemical disinfection reduces risk of infectious disease, but the interaction between chemical disinfectants and precursor materials in source water results in the formation of DBPs. Although disinfection of public drinking water has dramatically reduced outbreaks of diseases attributable to waterborne pathogens, the identification of chloroform, a DBP, in drinking water (Rook 1974; Bellar and Lichtenberg 1974) raised questions about possible health risks posed by these DBPs. Since 1974, additional DBPs have been identified, and concerns have intensified about health risks resulting from exposures to DBPs.

All natural waters and even treated drinking water exerts disinfectant demand due to the reactions with NOM and other constituents in water. Therefore, the applied disinfectant dose must be sufficient to meet the inherent demand in the treated water, to provide sufficient protection against microbial infection, and at the same time minimize exposure to DBPs.

Consequently, much research has been invested in attempting to characterize the nature of DBPs and the conditions that govern their formation in drinking water. One aspect of this research is the development of mathematical models for predicting the decay of chlorine and other disinfectants and for predicting the formation of DBPs themselves.

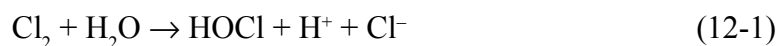
This chapter reviews current and historical research efforts related to the development of models for predicting the decay of disinfectants and the formation of DBPs. It focuses on chlorine as a disinfectant and emphasizes U.S. Environmental Protection Agency (EPA) research efforts in this area. The conditions that govern the interaction of NOM and chlorine and the resulting formation of DBPs are discussed. Research devoted to models for chlorine decay and the formation of DBPs are reviewed. The factors that affect exposure to DBPs are examined, and EPA field research studies that have driven the current research on chlorine decay and DBP formation are presented. The development of EPANET, a state-of-the-art public sector water quality/hydraulic model, is reviewed, along with the evolution of numerical modeling techniques. The topic of storage tanks and their impact on water quality and the public policy issues associated with this research is also discussed.

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Chemistry of Disinfectants in Water

In order to understand the nature of the risk tradeoffs associated with the loss of chlorine residuals and the formation of DBPs, it is necessary to review some of the chemistry involved in this process.

Chlorine dissolved in water yields the following (White 1999):



HOCl generally reacts with the various components that make up chlorine demand as follows:



Consequently, chlorine is consumed and chlorine residuals dissipate, which may then result in microbiological regrowth and which, in turn, may increase the system's vulnerability to contamination. Three factors which frequently influence chlorine consumption in drinking water are (1) reaction with organic and inorganic chemicals (e.g., ammonia, sulfides, ferrous iron, manganous ion, humic material) in the bulk aqueous phase; (2) reactions with biofilm at the pipe wall; and (3) consumption by the corrosion process.

A by-product of chlorination is the formation of total trihalomethanes (TTHMs) and other DBPs in waters containing organic precursor compounds, such as humic and fulvic acid substances. Generation of TTHMs has been shown to be a function of various water quality parameters and chlorination conditions including total organic carbon (TOC), the type of organic precursor, chlorination level, pH, temperature, bromide level, reaction time, and UV-254 absorbance. TTHMs are also regulated under the Safe Drinking Water Act (SDWA) and its amendments of 1986 and 1996 (Amy et al. 1987; Clark et al. 1996b). Chlorine decay in distribution systems is generally considered to consist of two components. One component is wall demand, while the other is associated with decay in the bulk phase of the water (Clark et al. 1993a).

Chlorine demand and the formation of DBPs are influenced by both the condition of treatment as well as the constituents in the raw and treated water. Treatment processes change the concentration of drinking water constituents and are likely to change the composition and characteristics of the water distributed to the consumer. Therefore, when modeling chlorine decay and the formation of DBPs, it is important to find modeling-input parameters which can reflect these changes in water quality characteristics. Some common surrogate parameters for NOM are TOC and spectral absorbance. TOC concentration is indicative of the mass of material, whereas spectral absorbance relates more to specific structure and functional groups. DOC is the dissolved fraction of TOC. For NOM, the most commonly used spectral absorbance is the ultraviolet (UV) absorbance (UVA) at a wave length of 254 nm (UVA) which measures conjugated double bonds. The specific UVA (SUVA) is the ratio of UVA to the DOC. Its values give an indication of the NOM's nature, with higher values indicating a more aromatic character (Amy 1993).

For most waters, the reactions of chlorine with NOM make up the majority of the chlorine demand. Chlorine also reacts with various inorganic compounds. For example, chlorine reacts with ammonia to form different species of chloramines. Aqueous chlorine converts Br^- into hypobromous acid (HOBr), which then attacks organic compounds to form brominated DBPs.

Chlorine will oxidize soluble iron and manganese to the insoluble ferric and manganic forms, respectively. Hydrogen sulfide reacts with chlorine, and successful removal of H_2S by conventional treatment with prechlorination has been reported.

Normally, the reactions between disinfectant and NOM make up the majority of the disinfectant demand and the subsequent formation of DBPs. The demand caused by inorganic or microbial demand is much less than the demand associated with NOM.

Some of the factors that influence both the formation of DBPs and the demand for chlorine are as follows:

- Disinfectant dose: several studies have shown that the formation of DBPs increases with chlorine concentration.
- Reaction time: a longer reaction time generally leads to both higher disinfectant demand and greater DBP formation.
- pH: For chlorine reactions, a shift in pH has little effect on chlorine demand. However, increase in TTHM formation has been observed with increases in pH. The sum of HAA6 (the sum of six of the nine haloacetic acid [HAA] species) has been found to decrease when pH increases.
- Temperature: An increase in temperature has been shown to cause an increase in the rate of both DBP formation and chlorine demand.

As mentioned previously, chlorine residuals are important to ensure the microbial safety of distributed drinking water. Requirements for disinfection of drinking water are defined in the Surface Water Treatment Rule (SWTR). According to the SWTR, treatment including disinfection must reliably achieve at least a 3-log (99.9%) removal and/or inactivation of *Giardia lamblia* cysts, and a 4-log (99.99%) reduction and/or inactivation of viruses prior to the delivery of water to the first consumer (Clark and Feige 1993). A control parameter frequently considered and specified in the SWTR is the CT (the product of the disinfectant residual concentration (mg/L) and contact time (min) measured at peak hourly flow) concept. Contact time is measured from the point of disinfectant application to the first customer (Clark and Feige 1993). Different disinfectants require different CT values because of their variability of action against different types of organisms. For example, chlorine is relatively ineffective against some protozoan, such as *Cryptosporidium*, but is generally very effective against most bacteria and viruses.

The SWTR requires that a minimum disinfectant level be maintained in all parts of a distribution system. Therefore, it is important that the factors that influence chlorine decay be identified and that models that can reliably predict chlorine residual levels in treated and distributed water be developed.

Modeling the Decay of Chlorine Residuals

A number of investigators have conducted research into the development of models to predict chlorine decay in drinking water. In one of the earliest attempts to model chlorine decay, Feben and Taras (1951) developed the following model:

$$D_t = D_1 t^n \quad (12-3)$$

In Equation 12-3, D_t = the chlorine consumed at time t (hr), D_1 = the chlorine consumed after 1 hour, and n is a constant characteristic of a given water. The 1-hour chlorine demand and n must be determined experimentally for a given water.

Haas and Karra (1984) investigated several models to describe chlorine decay, including

- First-order decay
- Power-law decay (n th order)
- First-order decay with stable components

- Power-law decay with stable components (n th order)
- Parallel first-order decay

They found that the parallel first-order decay model yielded the best results. This model assumes that there are two constituents in water that react with chlorine: (1) fast-reacting components, which exert an initial decay; and (2) slow-reacting components, which are responsible for long-term chlorine demand. This model was applied by Vasconcelos et al. (1997) in a project conducted jointly by EPA and the American Water Works Association Research Foundation (AWWARF) and is discussed later in this chapter.

A model by Qualls and Johnson (1983) described the short-term chlorine consumption by fulvic acids during the first 5 minutes of a reaction. This model (Equation 12-4) was originally developed for cooling water systems, but was then applied to disinfection of natural waters:

$$-dCl/dt = k_1[Cl][F_1] + k_2[Cl][F_2] \quad (12-4)$$

The chlorine decay is described by the sum of two first-order equations, in which the first part describes a rapid decay within the first 30 seconds, and the second simulates a slower decay from 30 seconds to 5 minutes. In Equation 12-4, $[Cl]$ is the free residual chlorine, k_1 and k_2 are rate constants for the fast and slow reactions, respectively, and $[F_1]$ and $[F_2]$ are the concentrations of reactive sites on the fulvic acids for the fast and slow reactions, respectively.

Hao et al. (1991) demonstrated that chlorine reacts with organic material as well as inorganic material by evaluating the kinetics of Mn(II) oxidation with chlorine and examined the effects of chlorine dose and the presence of complexing agents on chlorine demand. They found that Mn(II) oxidation is facilitated by excess chlorine at pH = 8. An autocatalytic model analogous to that for Mn(II) oxidation by O_2 was developed in which the major mechanism for Mn(II) removal was the heterogeneous Mn(II) adsorption onto newly precipitated MnO_2 . The same model also describes the effects of pH and the external addition of MnO_2 on Mn(II) removal.

Ventresque et al. (1990) conducted a study at the Choisy-le-Roi water treatment plant near Paris to identify the organic components that react with chlorine. The plant consists of preozonation, coagulation, sedimentation, sand filtration, ozonation, granular activated carbon (GAC) bio-adsorption, and post-chlorination. The water is dechlorinated before being distributed to the consumer. The authors applied a second-order kinetic model to the long-term chlorine demand data. They analyzed the kinetics at every stage of the plant and found that the initial chlorine demand and the kinetic constants of ozone/GAC-treated water were always lower than those obtained from sand-filtered water. These results demonstrated the effect of activated carbon on the removal of organic matter.

Jedas-Hecart et al. (1992) attempted to identify the organic compounds that react with chlorine from the Seine River entering the final treatment stage at the Choisy-le-Roi plant. They studied the chlorine consumption kinetics of samples of water taken after overall treatment. They divided the chlorine decay into two phases. An initial phase of immediate consumption during the first 4 hours was called the initial chlorine demand. The second, slower consumption phase after the first 4 hours was defined as the long-term demand (LTD). The LTD was interpreted with the following kinetic equation:

$$-\frac{dx}{dt} = k(a - x)^\alpha \left(b - \frac{x}{n}\right)^\beta \quad (12-5)$$

where x = chlorine consumption after 4 hours, k = the rate constant, a = the total residual chlorine at 4 hours, b = maximum potential chlorine demand, n = stoichiometry, and β = partial orders of reaction.

This model cannot be applied from time zero of chlorination because the LTD obeys a different reaction order than the initial chlorine demand.

The Water Treatment Plant (USEPA 1992) model described chlorine decay by dividing the decay curve into three components. These included an initial (t less than 5 minutes) reaction, a second-order reaction (5 minutes less than t less than 5 hours), and a first-order reaction (t greater than 5 hours). These equations apply only when the initial chlorine/TOC ratio is $\geq 1:1$.

Zhang et al. (1992) conducted a study of chlorine modeling in sand-filtered water (before post-chlorination) at the Macao treatment plant which draws water from the estuary of the West River (the main stream of the Pearl River in South China). The study indicated that the chlorine consumption in sand-filtered water can be divided into two phases: an initial chlorine consumption during the first hour which corresponds to the contact time in the reservoir of the treatment plant, and a long-term chlorine consumption after 1 hour in the network. This second component is interpreted in terms of an apparent first-order equation. According to the experiments performed on steel and asbestos cement pipes (diameter greater than 250 mm), the chlorine consumption by pipes is negligible. The authors suggested more experiments to be performed to verify the eventual influence of water velocity and diameter of pipe on the chlorine consumption by pipe itself. The chlorine disappearance in the network of Macao can be modeled as a first-order reaction.

To describe the entire disinfectant reaction for one ground water treated in a particular plant, Lyn and Taylor (1993) calculated the chlorine residual (CLR) as a function of chlorine dose, DOC, temperature, and time, using an empirical constant applicable only for that particular water.

Dugan et al. (1995) proposed a saturation model in order to predict the entire chlorine decay curve with one equation. TOC was chosen as the predictive water quality parameter for the saturation model because it represents the compounds exhibiting chlorine demand.

Chambers et al. (1995) conducted a study to test the validity of the exponential decay expression for free and total chlorine modeling using two sample networks and proprietary models. A sampling program was devised to collect information to calibrate the models. Rate constants for free and total chlorine were calculated. The results showed that the exponential decay model is appropriate for modeling chlorine in distribution systems and that it is possible to produce useful water quality models. They also showed that the rate constants for the water in the network were different from the rate constants collected in bench-scale experiments.

EPA Research Activities

The Water Supply and Water Resources Division (WSWRD) of EPA has been very active in conducting research into the factors that affect chlorine decay in drinking water. One of the first projects to investigate the feasibility of modeling water quality and chlorine decay in drinking water distribution systems was conducted under a cooperative agreement initiated between the North Penn Water Authority in Lansdale, Pennsylvania, and EPA (Clark and Coyle 1990; Clark et al. 1988a). The project provided the basis for development of a water quality model called the Dynamic Water Quality Model (DWQM) which was applied to several service areas in the South Central Connecticut Regional Water Authority (SCCRWA). An extensive field sampling study was conducted as part of the model validation and verification. Chlorine demand was calculated according to a first-order decay assumption, which is defined as follows:

$$C = C_0 e^{-kt} \quad (12-6)$$

where C = the concentration at time t , C_0 = initial chlorine concentration, k = decay rate in min^{-1} , and t = time in min.

It is clear that, as dissolved chlorine travels through the pipes in the network, it reacts with NOM in the bulk water and with biofilm and tubercles on the pipe walls or with the pipe wall material itself (Clark et al. 1993a). This reaction results in a decrease in chlorine residual and a corresponding increase in DBPs, depending on the residence time in the network and the holding time in storage facilities. An early study designed to address these issues using a complete water quality and hydraulics model was conducted by EPA in collaboration with the North Marin Water District in California (Clark et al. 1994). As a follow-on to the North Marin study, Vasconcelos et al. (1997) investigated the factors leading to loss of chlorine residual in several water distribution systems. Kinetic rate equations describing the decay of chlorine were developed, tested, and evaluated using data collected in field-sampling studies conducted at these water utility sites. These studies are discussed in more detail later in this chapter.

Clark (1998) developed an equation for chlorine decay based on the concept of competing reacting substances and on the assumption that the balanced reaction equation can be represented by



In Equation 12-7, if A and B are the reacting substances, a and b are the proportion of reacting substances, and P is the product of the reaction, then the rate of reaction is given by

$$\frac{dC_A}{dt} = -k_A C_A C_B \quad (12-8)$$

or

$$\frac{dC_B}{dt} = -k_B C_A C_B \quad (12-9)$$

or

$$\frac{dC_P}{dt} = k_P C_A C_B \quad (12-10)$$

Since both C_A and C_B are changing with time, a relation connecting them is written in order to integrate the differential equation. If C_{A0} and C_{B0} represent the initial concentrations of A and B , respectively, at $t = 0$ and x represents the concentration of A that has reacted, then the concentration of B that has reacted is given by bx/a . Consequently,

$$C_A = C_{A0} - x \quad (12-11)$$

and

$$C_B = C_{B0} - \frac{bx}{a} \quad (12-12)$$

From Equation 12-12

$$dC_A = -dx \quad (12-13)$$

and

$$-dC_A = \frac{bx}{a} \quad (12-14)$$

By substituting in Equation 12-8 and rearranging:

$$\frac{dC_A}{(C_{A_0} - x)(C_{B_0} - bx/a)} = k_A dt \quad (12-15)$$

Integrating Equation 12-15 and making the appropriate substitution yields

$$C_A = \frac{K}{1 - Re^{-ut}} \quad (12-16)$$

In Equation 12-16, C_A is the concentration of free chlorine. Rewriting Equation 12-16 yields

$$Cl(t) = \frac{K}{1 - Re^{-ut}} \quad (12-17)$$

where $Cl(t)$ = the chlorine concentration in mg/L at time t ; R (dimensionless), K (mg/l), and u (min^{-1}) are parameters to be estimated; and t = the time of reaction in minutes. In Equation 12-17, the value for the rate constants can be rewritten as follows:

$$u = M(1 - K) \quad (12-18)$$

where

$$M = \frac{k_A b C_{A_0}}{a} \quad (12-19)$$

Equation 12-16 was applied to a series of data sets collected from the Vasconcelos et al. (1997) study.

Clark and Sivaganesan (1998) utilized the equation developed by Clark (1998) to predict chlorine decay and TTHM formation in a number of field and laboratory data sets. The parameters for Equation 12-16 are estimated using regression analysis. Predictive equations were developed for the parameters K , M , and R based on initial chlorine concentration (C_{A_0}), pH, TOC, and temperature ($^{\circ}\text{C}$). The estimated parameters for Equation 12-16 are as follows:

$$K = e^{0.32(C_{A_0})^{-0.44}(\text{TOC})^{0.63}(\text{pH})^{-0.29}(\text{Temp})^{0.14}} \quad (12-20)$$

$$K = e^{1.49(C_{A_0})^{-0.48}(\text{TOC})^{0.18}(\text{pH})^{0.96}(\text{Temp})^{0.28}} \quad (12-21)$$

and

$$\text{Log}_e(M) = -2.46 - (0.19 \text{ TOC}) - 0.14 \text{ pH} - (0.07 \text{ Temp}) + (0.01 \text{ Temp} * \text{pH}) \quad (12-22)$$

The estimated Model R^2 s are 0.71, 0.78, and 0.42, respectively, for these equations. The model was validated against data collected from two field studies. Using standard statistical techniques, the upper and lower 95% confidence intervals were calculated for each parameter.

Rossman et al. (1999) examined the factors that characterize the reaction conditions affecting treated water in a distribution system. Some of these factors are the pipe wall material, such as corrosion

products and biofilm slime, which can exert a significant chlorine demand. If chlorine is being consumed within a pipe by non-DBP-producing materials (such as ferrous corrosion products), then there is less available to react with the water's NOM. However, iron tubercles have also been shown to contain organic material that might include DBP precursors. Much of the study was devoted to studying the rate at which DBPs form in a pipe as compared to a glass bottle. One of the conclusions from the study was that the rate constants for chlorine decay in the pipe were an order of magnitude higher than in the bottle.

As an extension to their previous research, Clark and Sivaganesan (in press) hypothesized that two competitive reactions would adequately describe chlorine decay in raw and finished water. One reaction was assumed to represent the fast-reacting components associated with chlorine decay, and the second reaction was assumed to represent the slower-reacting components. In order to test this hypothesis, a model consisting of two competitive reactions was developed as described below:



where C_A^1 is the free chlorine residual reacting with the collection of rapidly reacting components C_B^1 ; C_A^2 is the free chlorine residual reacting with the collection of more slowly reacting components C_B^2 ; P^1 and P^2 are a collection of the by-products of the two reactions; and $a_1, b_1, p_1, a_2, b_2,$ and p_2 are the stoichiometric coefficients. These equations can be used to quantify the fraction of initial chlorine being utilized by the fast- and slow-reacting components.

The expressions below describe the change in C_A^1 and C_A^2 with time (Clark and Sivaganesan 1998):

$$C_A^1(t) = \frac{Cl_0^1(1 - R_1)}{1 - R_1 e^{-(1-R_1)k_1 t}} \quad (12-25)$$

$$C_A^2(t) = \frac{Cl_0^2(1 - R_2)}{1 - R_2 e^{-(1-R_2)k_2 t}} \quad (12-26)$$

where Cl_0^1 and Cl_0^2 are the initial concentrations of C_A^1 and C_A^2 ; $C_A^1(t)$ and $C_A^2(t)$ represent the change in the concentration of C_A^1 and C_A^2 with time; $k_1, k_2, R_1,$ and R_2 are parameters in Equations 12-25 and 12-26; and t represents time. The total initial chlorine concentration at time = 0 is

$$Cl_0 = Cl_0^1 + Cl_0^2 \quad (12-27)$$

where Cl_0 is the total initial chlorine residual. If Cl_0^1 and Cl_0^2 are the initial concentrations of chlorine reacting in Equations 12-23 and 12-24, then

$$Cl_0^2 = Cl_0 - Cl_0^1 \quad (12-28)$$

The equation for the complete reaction is assumed as the sum of Equations 12-25 and 12-26 or

$$Cl(t) = \frac{Cl_0^1(1 - R_1)}{1 - R_1 e^{-(1-R_1)k_1 t}} + \frac{(Cl_0 - Cl_0^1)(1 - R_2)}{1 - R_2 e^{-(1-R_2)k_2 t}} \quad (12-29)$$

Given that Cl_0 is known and that Cl_0^1 , k_1 , k_2 , R_1 , and R_2 are unknowns, Equation 12-29 yields a five-parameter equation as follows:

$$Cl(t) = \frac{Cl_0 Z(1 - R_1)}{1 - R_1 e^{(1-R_1)k_1 t}} + \frac{Cl_0(1 - Z)(1 - R_2)}{1 - R_2 e^{(1-R_2)k_2 t}} \quad (12-30)$$

where $Cl(t)$ is the residual chlorine at t hours, and $Z = (Cl_0^1 / Cl_0)$, k_1 , k_2 , R_1 , and R_2 are unknown parameters. All the model parameters are positive, and Z cannot be larger than 1.

The SAS procedure NLIN was used (SAS 1990) to estimate the model parameters. Since there is more than one solution to the above model and since the solutions depend on the initial values, model parameters were estimated in three steps to stabilize the solution. First, residual chlorine (Cl_t) values from the first 60 minutes (generally 4–6 data points) were used to estimate the parameters R_1 and k_1 in Equation 18. The next step was to fix k_1 at its estimated level and then use all the residual chlorine values to estimate Z , R_1 , R_2 , and k_2 in Equation 12-30. Finally, the estimated Z , R_2 , and k_2 values from Equation 12-30 were fixed, and the remaining model parameters R_1 and k_1 were re-estimated using data from the first hour of the experiment.

Thirty seven raw water data sets and twelve treated water data sets were used to develop a general model. The five model parameters were then regressed against TOC level, initial UVA level (UVA_0), initial chlorine level (Cl_0), pH, initial bromide level (Br^-), temperature (Temp) in °C, and alkalinity in mg/L (ALK). The following general multiplicative model was used for each of the parameters: k_1 , k_2 , R_1 , R_2 , and $Z/(1 - Z)$:

$$Y = c(TOC + 1)^d(UVA + 1)^e(Cl_0 + 1)^f(pH)^g(Br^- + 1)^h(Temp)^i(ALK)^j \quad (12-31)$$

where Y = the parameter value, and c , d , e , f , g , h , i , and j are the exponents. Equation 12-31 can be rewritten as

$$\log(Y) = \log(c) + d\log(TOC + 1) + e\log(UVA + 1) + f\log(Cl_0 + 1) + g\log(pH) + h\log(Br^- + 1) + i\log(Temp) + j\log(ALK) \quad (12-32)$$

The SAS procedure “REG” is used to estimate the model parameters in Equation 12-32 (SAS 1992). This model guarantees that the predicted parameters are positive. Only parameters at the 5% level of significance were included in the model. Influential analysis was used to identify the data points which have a major impact on the parameter estimates. If the absolute value of the standardized residual of a data point was larger than 3, then that point was not included in the statistical analysis for any of the five model parameters (Equation 12-30). The resulting parameter-estimating equations are as follows:

$$k_1 = e^{6.58} (TOC + 1)^{2.66} (UVA + 1)^{7.63} (Cl_0 + 1)^{-3.25} (pH)^{-1.45} (Br^- + 1)^{0.06} \quad (12-33)$$

$$R_1 = e^{-3.56} (TOC + 1)^{1.68} (UVA + 1)^{3.94} (Cl_0 + 1)^{-1.68} (pH)^{1.05} (Temp)^{0.69} \quad (12-34)$$

$$Z/(1 - Z) = e^{4.94} (UVA + 1)^{2.89} (Cl_0 + 1)^{-0.57} (pH)^{-1.16} (Temp)^{-0.79} \quad (12-35)$$

$$k_2 = e^{-4.83} (TOC + 1)^{-2.43} (UVA + 1)^{-7.71} (Cl_0 + 1)^{3.63} (Br^- + 1)^{-0.32} (Temp)^{-0.31} (ALK)^{0.14} \quad (12-36)$$

$$R_2 = e^{0.48} (TOC + 1)^{1.81} (Cl_0 + 1)^{-1.82} e^{0.03 \cdot Temp} \quad (12-37)$$

The model R^2 are 0.60, 0.67, 0.57, 0.58, and 0.52, respectively. The model was applied to various data sets in order to test its application, and it was found that, in general, the model fits the experimental data well.

Modeling the Formation of DBPs

Trusell and Umphres (1978) reviewed the effect of preozonation, bromide, pH, and chlorine dose on the formation of TTHMs in natural waters and proposed a kinetic model that describes their formation. They concluded that some of the factors that might influence the rate of the TTHM reaction are pH, temperature, the level of precursor, the level of chlorine, and the level of bromide ion before chlorine addition. They proposed two equations—one describing the rate of chlorine (Cl) consumption and one describing the rate of reduction of precursor or, conversely, the rate of TTHM production. Assuming that the reaction between chlorine residual and aquatic humic material is related to the concentration of each, a simple relation is obtained for the rate of chlorine consumption.

$$\frac{d[Cl_2]}{dt} = -k_1[Cl_2][TOC] \quad (12-38)$$

If it is assumed that the action of the chlorine does not significantly reduce the total concentration of the humic precursor, then the following equation represents the rate of TTHM production and is first order with respect to chlorine residual:

$$\frac{dTTHM}{dt} = -\frac{dC}{dt} = k_2(Cl_2)(C)^m \quad (12-39)$$

where m is the order of reaction with respect to the precursor concentration and C is the concentration of the organic precursor. The authors concluded that there are a number of factors of importance in describing the formation of TTHMs including the nature of aquatic humus, the influence of preozonation on TTHM formation, the influence of bromide, the influence of pH, and the influence of chlorine dose.

Kavanaugh et al. (1980) developed a two-parameter kinetic model for predicting THM formation in the distribution system following post-chlorination. They hypothesized that THM formation can be described by the overall stoichiometric expression



where $A = HOCl$, $B = TOC$, and $C = TTHM$, while the n th overall rate constant for the reaction is k_n . Based on this expression, three moles of hypochlorous acid react with one mole of carbon in the organic precursor material to form one mole of TTHM. The rate expression for the formation of TTHM is given by

$$\frac{dC}{dt} = k_n(B)(A)^m \quad (12-41)$$

assuming that the rate of formation is first order with respect to TOC and m th order with respect to HOCl. The chlorine concentration A can then be related stoichiometrically to C by defining a TTHM yield as the moles of TTHM formed per mole of Cl_2 consumed. The rate expression then becomes

$$\frac{dC}{dt} = k_n(B[A_0 - \frac{3C}{f}])^m \quad (12-42)$$

When the free chlorine is exhausted

$$f = \frac{3C}{A_0} \quad (12-43)$$

the yield f can be determined by measuring the THM concentration when $A = 0$. The equation is therefore a three-parameter kinetic model with k_n as the rate constant, m the reaction order with respect to Cl_2 , and f the TTHM yield which must be determined empirically for the particular system under investigation.

Amy et al. (1987) discussed the formulation and calibration of several models for predicting TTHMs in untreated natural waters subjected to chlorination. Their general approach was to analyze specific portions of a large database derived from several natural water sources in order to isolate the effects of a given parameter on TTHM formation. Two general strategies were used in formulating the models: multiple linear regression models using logarithmic transformations of both independent and dependent variables and multiple nonlinear regression models, which were also developed. Both models assume that a chlorine residual is maintained throughout a 168-hour reaction period and that TTHMs continuously increase with time. Variables such as UV absorbency, chlorine dose, temperature, and TOC were used to predict TTHMs.

McKnight and Reckhow (1992) investigated the reactions of specific ozone by-products (OBPs) with chlorine and chloramines through evaluation of the kinetics and stoichiometry of chlorine demand and total organic halide (TOX) formation as a function of pH. All of the compounds studied had a carbonyl ($\text{C} = \text{O}$) functionality, causing the types of chemical reactions to be similar. Simple compounds were chosen from among the carbonyl compounds, aldehydes, ketoaldehydes, and keto-acids in order to study the relationships between structural characteristics and reactivity towards chlorine and chloramines. Three general classifications of alpha substituents were made: compounds bearing (1) an alpha methyl group; (2) methylene group; or (3) other moieties (hydrogen, hydroxyl, carboxylic acid, etc.). Correlations were developed between these characteristics and chlorine consumption behavior to help in understanding the significance of OBP formation in distribution systems (i.e., persistence of OBPs, formation of chloroform or other DBPs, etc.).

Little or no TOX was produced upon chloramination of all the model compounds studied in this research. Results suggest that acetaldehyde, methyl glyoxal, and pyrovic acid could be important chloroform precursors in chlorinated systems under certain conditions. The higher aldehydes studied reacted slowly with free chlorine and produce minor amounts of TOX. The keto-acids reacted rapidly with both free and combined chlorine. Chloramination of the model OBPs studied resulted in little measurable TOX formation. The rates for chlorination and chloramination at pH 7 were comparable for all three compound classes, but the rates of chlorination increased dramatically with pH. Chloramination rates appear to be only weakly dependent upon pH. These results suggest that aldehydes may persist in distribution systems at low (less than 2 mg/L) chlorine doses and neutral pH, but can undergo significant decomposition at higher chlorine doses and pH. The keto-acids are likely to react rapidly at low chlorine doses and pH 7 or greater. These compounds may also be generated in distribution systems by the reactions of disinfectants with NOM, and their by-products may be sources of assimilable organic carbon (AOC); thus, their presence in a distribution system may be of concern.

Harrington et al. (1992) developed a computer program to simulate DBP formation, removal of NOM, inorganic water quality changes, and disinfectant decay in water treatment processes. Equations were developed that simulate the formation of TTHMs and removal of TOC and UVA by alum coagulation, as well as changes in alkalinity and pH. Model simulations were compared with limited sets of observed values. The central tendency of the model was to underpredict finished-water pH by 4 percent, finished-water TOC by 7 percent, and simulated distribution system TTHMs by 20 to 30 percent.

Shukairy et al. (1994a) conducted a study with the objective of better understanding the chlorination reactions of organic matter by investigating the formation of halogenated DBPs from three molecular-sized (MS) fractions as follows: greater than 3000, 1000–3000, and less than 1000 daltons. The study

was conducted in two phases. In Phase I, the impact of ozonation and biotreatment on DBP precursors under variable reaction conditions was evaluated, and in Phase II, the chlorination kinetics and reactivity of these fractions under constant organic and inorganic precursor concentrations was investigated.

The impact of organic and inorganic precursor limitations on the reactivity and kinetics of halogenated DBPs was also evaluated. It was found that the less-than-1K MS fraction was the most biodegradable fraction and the 1-3K MS fraction the least. Preozonation resulted in chemical transformation of the organic matter, resulting in an increase in biodegradability in all fractions and in a decrease in the reactivity to subsequent chlorination. Biotreatment, with and without ozonation, resulted in equivalent removal of the DOC and the precursor compounds, as no selectivity was observed. They found that, under variable precursor concentrations, the speciation of the THMs was dependent on the bromide-to-DOC ratio. Increases in this ratio resulted in a shift in speciation to the bromo-substituted DBPs, irrespective of the fraction or the treatment. Precursor limitation did not affect the reaction kinetics significantly. However, the yield and the reactivity were affected. Speciation depended on the available organic matter. The less-than-1K MS fraction, under constant precursor concentrations, exhibited the fastest chlorination kinetics as measured by the higher chlorine demand, TTHM, and HAA6 kinetics. The less-than-1K fraction also exhibited the highest reactivity to bromo-substitution.

Cowman and Singer (1996) investigated the effect of bromide ion on the distribution of HAA species resulting from the chlorination and chloramination of waters containing aquatic humic substances. Aquatic humic substances were extracted from both a surface water and a ground water. They were chlorinated and chloraminated at pH levels of 8 and 6 in the presence of bromide concentrations ranging from 0 to 25 $\mu\text{g/L}$. The samples were analyzed for all nine of the HAA species containing bromine and chlorine. Standards for bromodichloroacetic acid and dibromochloroacetic acid were synthesized for use in this study. It was found that bromochloro-, bromodichloro-, and dibromochloroacetic acids formed easily and constituted at least 10% of the total HAA concentration in waters containing as little as 1.2 μM (0.1 mg/L) bromide. At concentrations normally found in raw drinking water, the mixed bromochloro HAA species were major components of the total HAA concentration. Among the mono-, di-, and trihalogenated forms, the distribution of HAAs appeared to be independent of bromide concentration.

Shukairy and Summers (1992) conducted a study to examine the impact of ozonation and biotreatment on organic precursor characteristics established by evaluating DBP formation, speciation, and kinetics under constant DOC, bromide, and chlorination conditions. The following observations were made:

- Use of ozone resulted in a significant change in the characteristics of the organic matter.
- Treatment, ozonation, or biotreatment decreased chlorine demand, indicating selective oxidation of the organic precursors.
- In nearly all cases, treatment resulted in a decrease in DBPs formed after chlorination. In most cases, TOX and total THM formation decreased more by ozonation and ozonation/biotreatment in comparison to biological treatment, indicating that chemical oxidation of organic matter decreased its reactivity.
- HAA6 formation decreased the most by biotreatment, with and without preozonation. Biotreatment appears to be selective for HAA precursors.
- Spectral absorption coefficient (SAC) decreased significantly after ozonation, resulting in less available reactive aromatic unsaturated organic precursors than in the control, even when the DOC concentration was held constant. The reactive aliphatic (acetyl-)containing precursors created after ozonation seem to favor bromine substitution over chlorine substitution.
- Precursor limitation is very important in determining speciation. In the case where the reaction is precursor limited, bromine substitution is faster than chlorine substitution and will govern the DBP speciation. The formation of chloro-substituted DBPs continues as long as there are available precursors and thus controls DBP distribution. They found that, under

conditions of constant bromide, DOC, chlorination conditions, and holding times, biotreatment did not show any selectivity for DBP precursors, that is, DOC and the precursors were removed to the same extent.

Shukairy (1994) and Shukairy and Summers (1996) conducted a study to examine the impact of ozonation and biotreatment on the organic precursor characteristics by evaluating DBP formation, speciation, and kinetics under constant DOC, bromide, and chlorination conditions. The following observations were made:

- Ozonation resulted in a significant change in the characteristics of the organic matter. SAC decreased while DOC concentration was nearly unchanged, indicating a decrease in UV-absorbing functional groups and the formation of saturated and aliphatic acetyl compounds. Biotreatment resulted in equivalent removal of both SAC and DOC.
- Treatment, ozonation, or biotreatment decreased chlorine demand, indicating selective oxidation of the organic precursors, either chemical or biological.
- In nearly all cases, treatment resulted in a decrease in DBPs formed after chlorination.
- In most cases, TOX and total THM formation decreased more by ozonation and ozonation/biotreatment in comparison to biological treatment, indicating that chemical oxidation of organic matter decreased its reactivity.
- HAA6 formation decreased the most by biotreatment, with and without preozonation. Biotreatment appears to be selective for HAA precursors. However, such a conclusion is only tentative as the decrease in HAA concentration could be due to a shift to the other three more bromo-substituted HAA species that are not quantified.
- Speciation was affected most by ozonation. A shift to bromo-substituted species occurred after ozonation and after combined ozonation/biotreatment.
- No such shift was observed by biotreatment alone. Bromine incorporation factors increased significantly with ozonation. The effect was most pronounced at 6 hours. As the holding time was increased, more TTHM, Cl and HAA6-Cl were formed, increasing DBP formation. The relative increase in DBP-Br with increasing holding time was much smaller.
- SAC decreased significantly after ozonation, resulting in less available reactive aromatic unsaturated organic precursors than in the control, even when the DOC concentration was held constant. The reactive aliphatic (acetyl-)containing precursors created after ozonation seem to favor bromine substitution over chlorine substitution. For the THMs and quantifiable HAAS, DBP-Br formation increased while DBP-Cl formation was much less, relative to the control, because of decreases in the organic precursors.
- Precursor limitation is very important in determining speciation. In the case where the reaction is precursor limited, bromine substitution is faster than chlorine substitution and will govern the DBP speciation. The formation of chloro-substituted DBPs continues as long as there are available precursors and thus controls DBP distribution.

Shukairy and Summers (1996) found that, under conditions of constant bromide, DOC, chlorination conditions, and holding times, biotreatment did not show any selectivity for DBP precursors, that is, DOC and the precursors were removed to the same extent. Ozonation, however, had more of an impact on the organic matter characteristics, as observed by decrease in DBP formation (reactivity) and a shift to the bromo-substituted compounds. Precursor limitations are important in assessing DBP speciation; both DOC and SAC are important parameters that should be considered in evaluating organic precursors.

Shukairy (1998) investigated ozonation and biological treatment as a means of controlling the formation of DBPs as measured by TOX and purgeable organic halides (POX). Organic matter from a ground water and a river water source was used. Chlorine or chloramines were used as the final disinfectant. Chloramination produced significantly fewer organic halides, especially POX, compared to chlorina-

tion. With both disinfectants and for both sources of organic matter, the nonpurgeable organic halide formation rate was found to be much faster than that of POX. Preozonation decreased the amount of organic halide formation by 10 to 40% upon subsequent chlorination. With chloramines, preozonation had no significant impact on the extent of the reaction. Preozonation followed by biotreatment resulted in the least amount of organic halide formation, with a reduction of 50 to 80% when chlorine was used and greater than 90% with chloramines. In all cases, the ratio of organic halides to DOC decreased after biological treatment, indicating a selectivity for the potential reactive sites.

Shukairy (1998) found biodegradation to be very effective for controlling organic halide concentrations. The precursor concentrations were decreased, and the microorganisms seemed to be selective in biodegrading the moieties that are prone to substitution by the chlorine. Biodegradation of nonprecursor compounds may have also occurred, but not to complete mineralization, i.e., no change in DOC. While ozonation yields its own DBPs, e.g., aldehydes and ketones, subsequent biotreatment should help in the removal of these highly oxidized lower-molecular-weight compounds, many of which are biodegradable. In some cases, ozonation followed by biotreatment decreased purgeable organic halide formation potential (POXFP) and total organic halide formation potential (TOXFP) more than the sum of the decrease by the individual treatments, indicating a synergetic effect. Chloramines, which have been found to be as effective as free chlorine in killing attached bacteria in the distribution system, were shown to yield the lowest level of organic halides. Using ozonation followed by biotreatment would decrease the available substrate for microbial regrowth and provide primary disinfection. Smaller amounts of chlorine or chloramines could then be applied to provide adequate post-disinfection and a residual for the distribution system, therefore controlling the DBP concentration in finished water. The authors concluded that further investigations into the impact of biotreatment on individual DBPs is warranted. Similarly, the impact of ozone doses on biotreatment and DBP formation should be investigated to optimize the synergy of these processes. In addition, for both sources of organic matter, the formation rate of nonpurgeable organic halide (NPOX) is much faster than that for POX after either chlorination or chloramination.

- The majority of organic halide formation occurs at disinfectant doses less than 2 mg disinfectant per mg. DOC chloramination significantly decreased the organic halide formation, especially POX, compared to that formed by chlorination or ozonation/chlorination.
- Preozonation significantly decreased the amount of organic halides formed after chlorination, but had no impact on the organic halides formed after chloramination.
- Biological treatment alone and, more effectively, preozonation followed by biological treatment selectively reduced the organic halide precursor compounds compared to the overall background organic matter as measured by DOC.

EPA Research Activities

EPA research into the factors that affect chlorine decay and the formation of DBPs has ranged from pilot-plant studies that have investigated the role of ozone on brominated DBPs to the effect of corroded pipe on the formation of TTHMs and HHA6. Also included in these efforts is research on mutagenicity as a possible DBP and an attempt to define exposure research as it relates to the DBP problem.

Shukairy et al. (1994b, 1995) studied the effect of variable ozone dosage and bromide concentration on the formation of organic DBPs and bromate. Low-ozone dosages resulted in oxidation of organic precursors, yielding decreases in the formation potential for TTHMs, six HAAs, and TOX. Increasing the ozone dosage oxidized bromide to bromate, decreasing the bromide for incorporation into DBPs. Bromate concentrations were linearly correlated with ozone residuals. Changes in the bromine incorporation factors reflected differences in the resulting speciation of THMs and HAAs, respectively. Because

TOX measurements based on chloride equivalence may underestimate the halogenated DBP yield for high-bromide waters, they describe a procedure whereby bromide and bromate concentrations were used to correct the TOX measurement.

The effect of bromide concentration, ozone dosage, and biotreatment on the control of DBPs was also evaluated. Although TTHM precursors were better controlled by ozonation and the precursors of six HAAs were better controlled by biological treatment, the combined processes were effective for the control of all halogenated DBP precursors. Ozone's conversion of bromide to bromate and the chemical or biological oxidation of organic matter changed the ratio of bromide to DOC. Increases in this ratio increased the formation of some brominated DBPs, but these DBP increases were offset by the precursor oxidation provided by the combination of the two processes.

Clark et al. (1996b) developed a first order model to characterize the formation of brominated DBPs. Using a data set generated by Pourmoghaddas et al. (1993), models were developed that describe the formation of THM and non-THM chlorination by-products and their speciation. The model which considered pH, time, chlorine, and bromide concentration demonstrates the effect of bromide concentration on the formation of CHCl_3 and CHBr_3 . The model shows that the concentrations of CHBr_2Cl and CHBrCl_2 increase to a maximum for bromide concentrations of 2.5 mg/L and 0.5 mg/L, respectively, and then decline with increasing bromide levels. Concentrations of CHCl_3 consistently decline with increasing bromide concentration, while CHBr_3 consistently increases with increasing bromide concentration.

As a complement to his work on chlorine decay modeling, Clark (1998) developed a TTHM formation model based on chlorine consumption as follows:

$$\text{TTHM} = T(C_{A_0} - [\frac{C_{A_0}(1-R)}{1 - Re^{-ut}}]) \quad (12-44)$$

where

T = dimensionless parameter
 C_{A_0} = the initial chlorine residual in mg/L
 R = dimensionless parameter from the chlorine decay equation
 u = the reaction rate in time^{-1}
TTHM = total trihalomethanes

Clark and Sivaganesan (1998) verified this equation using both field and laboratory data from the study by Vasconcelos et al. (1997) and from laboratory data collected by the WSWRD of EPA.

Schenck et al. (1998) conducted a study to assess the applicability of the model developed by Vartiainen and Liimatainen (1988) to source waters and water treatment practices in the U.S. The model is based on data collected in Finland and relates mutagenicity, as determined in the Ames assay, to TOC concentration of the water, chlorine dose, and to a minor extent, the concentration of ammonia. It has been used as the basis for recent epidemiological studies conducted in Finland that have reported a positive correlation between the mutagenicity of chlorinated drinking waters and certain human cancers. In the work by Schenck et al. (1998), water samples were collected from three full-scale treatment plants and one pilot-scale plant in the U.S. All the plants used chlorine exclusively for disinfection. One full-scale plant used ground water; surface water sources were used by the other plants. TOC and ammonia concentrations were determined analytically, and chlorine doses were obtained from the treatment plants. The water samples were concentrated by resin adsorption for testing in the Ames assay. The observed levels of mutagenicity in the finished waters were 1.5 to 2.0-fold higher than those predicted using the

Vartiainen and Liimatainen (1988) model. The authors concluded that further validation was needed before the Finnish model could be used to assess exposure to mutagenicity in chlorinated drinking waters in the U.S.

Rossman et al. (1999) examined the factors that characterize reaction conditions affecting treated water in a distribution system versus reaction kinetics as determined in bench studies. Included among these factors are the pipe wall material, such as corrosion products and biofilm slime, which can exert a significant chlorine demand. If chlorine is consumed within a pipe by non-DBP-producing materials (such as ferrous corrosion products), then there is less available to react with the NOM in the water. Some of the factors that may contribute to differences in the rate of DBP formation in a pipe versus bench scale experiments are

- Iron tubercles which contain organic material that might include DBP precursors.
- The organic matrix supporting the growth of biofilm on pipe surfaces may also contain precursors.
- Certain DBPs, such as dichloroacetic acid, are biodegradable.
- The rate at which reactants are transported between the bulk flow and the reaction region near the pipe wall is affected by hydrodynamic conditions within the pipes.

The authors conducted a study to measure the rate of formation of two classes of DBPs in a simulated pipe environment and compared it with rates observed for the same water held in glass bottles. The DBPs studied were THMs and HAAs, both of which are currently regulated by EPA under its Disinfectants/Disinfection By-Products Rule. The simulated pipe environment is located at the EPA Test and Evaluation (T&E) Facility in Cincinnati, OH, and is designed to replicate actual flow conditions within a ductile iron pipe. The pipes used in this test had been subject to significant corrosion and biofilm buildup. The authors found that the production of THM and HAA in the pipe kept pace with that formed in the bottle given that the rate constants of chlorine consumption in the pipe (by mainly non-precursor material) were more than ten times higher than in the bottle. This suggests that chlorine is not a rate-limiting factor in the reactions that produce these compounds for the waters tested. The fact that a small, but consistently higher level of THM was produced in the pipe compared to the bottle for the same reaction time could be due to two reasons. First, the metallic surface of the pipe wall could serve as a catalyst for the THM formation reaction. Second, there could be THM precursors in the scale, tubercles, or biofilm attached to the pipe wall.

To test the second of these hypotheses, another set of experiments was performed with the pipe loop. This time the test water was chlorine demand-free, DBP precursor-free water derived from Cincinnati tap water. This water receives activated carbon treatment at the Cincinnati Water Works and was treated again on-site with a GAC canister to remove any residual chlorine, DBPs, and possible DBP precursors. Experiments were conducted with this water chlorinated to three different levels, without any initial holding time in the feed tanks. The results confirm that there must be a reservoir of precursor material attached to the pipe wall that is available to contribute to the formation of THMs. Results from their experiments led to the following conclusions:

- The rate constants for chlorine decay in the pipe were an order of magnitude higher than in the bottle.
- The high rate of chlorine loss in the pipe did not decrease the rate at which DBPs were produced when compared to the bottle.
- THM4 production in the pipe averaged 15 percent higher than in the bottle over a 24-hour period.
- The distribution of THM species over time, as reflected by the Bromine Incorporation Factor, remained similar between the pipe and the bottle.

- The rate of HAA6 production in the pipe was essentially the same as in the bottle.
- The test pipe contains a reservoir of precursor material on its walls that is available to form THMs.

As an extension of the research conducted by Clark et al. (1996b), Pourmoghaddas et al. (1993), Clark (1998), and Clark and Sivaganesan (1998) discussed previously, Clark et al. (2001) developed a general DBP formation model which is given as follows:

$$DBP_i = A_i \left[C_{A_0} - \frac{C_{A_0}(1 - K)}{1 - Ke^{-M(1-K)t}} \right] \quad i = 1, 2, \dots, 13 \quad (12-45)$$

where DBP_i = the specific disinfectant by-product subspecies being modeled in micromoles/liter; M , K , t , and C_{A_0} are as defined previously; and A_i is the ratio in micromoles/liter of by-product i formed to mg/L of chlorine consumed.

Several functional relationships were examined in an attempt to find a general model to predict K , M , and A_i in Equation 12-45. The variables pH , Br^- , Cl_0 , and P

(where $P = \frac{mBr^-}{(mCl_0 + mBr^-)}$, mCl_0 = moles of initial chlorine, and mBr^- = moles of bromide ion) were utilized in various combinations to develop predictive equations for these parameters. A general model for A_i was developed for chlorinated, mixed species and brominated compounds.

A multiple regression analysis for M yielded the following model shown below:

$$M = e^{a_1} e^{b_1 Br^-} e^{c_1 (Cl_0 * pH)} C_0^{d_1} e^{e_1 P} e^{f_1 pH} \quad (12-46)$$

where a_1 , b_1 , c_1 , d_1 , e_1 , and f_1 are parameters to be estimated. In Equation 12-46, e^{a_1} is a constant, $e^{b_1 Br^-}$ accounts for the impact of bromide concentration, $e^{c_1 (Cl_0 * pH)}$ accounts for the interaction of chlorine (mg/L) and pH, $C_0^{d_1}$ accounts for the impact of chlorine concentration alone in mg/L, $e^{e_1 P}$ accounts for the ratio of bromide in moles to bromide plus chlorine in moles, and $e^{f_1 pH}$ accounts for the impact of pH alone.

A multiple regression model for $\log(K)$ with $\log(pH)$, $\log(Br^-)$, and $\log(Cl_0)$ as the predictor variables yielded the equivalent multiplicative model as shown below:

$$K = e^{a_2} (pH)^{b_2} (Br^- + 1)^{c_2} (Cl_0)^{d_2} \quad (12-47)$$

where a_2 , b_2 , c_2 , and d_2 are parameters to be estimated. The first term in Equation 12-47, e^{a_2} , is a constant, $(pH)^{b_2}$ reflects the impact of pH, $(Br^- + 1)$ reflects the impact of bromide concentration in mg/L, and $(Cl_0)^{d_2}$ accounts for the impact of chlorine concentration in mg/L.

A multiple regression model for $\log(A_i)$ yielded the equivalent multiplicative model shown below:

$$A_i + a^i = e^{a_3^i} (pH)^{b_3^i} (Cl_0)^{c_3^i} (P + a^i)^{d_3^i} \exp[e_3^i Br^- + f_3^i (Br^-)^2 + g_3^i (Br^-)^3] \quad \forall i = 1, \dots, 13 \quad (12-48)$$

where a_3^i , b_3^i , c_3^i , d_3^i , e_3^i , f_3^i , and g_3^i are parameters to be estimated, and a^i takes on the value 0.0001 or 1.

In Equation 12-48, the first term on the right hand side ($e^{a_3^i}$) is a constant, $(pH)^{b_3^i}$ accounts for the effect of pH, $(Cl_0)^{c_3^i}$ reflects the impact of chlorine, and $(P + a^i)^{d_3^i}$ accounts for the impact of the molar ratios of bromide to bromide plus chlorine. The last term, $\exp[e_3^i Br^- + f_3^i (Br^-)^2 + g_3^i (Br^-)^3]$, was selected to represent the probability of bromine incorporation into the brominated, chlorinated, and mixed species

compounds considered in this analysis. In Equation 12-48, a^i is set equal to 1 for chlorinated compounds and is otherwise 0.0001.

Using data from Pourmoghaddas et al. (1993), least squares estimates for the parameters were calculated. The estimated parameters for K and M are given in Equations 12-49 and 12-50, respectively, as shown below:

$$M = e^{3.96} \cdot e^{-0.305(Br^-)} \cdot e^{0.0145(Cl_0 \cdot \text{pH})} \cdot Cl_0^{-2.32} e^{8.46(P)} e^{-0.231\text{pH}} \quad (12-49)$$

$$K = e^{1.89} \cdot (\text{pH})^{-0.13} \cdot (Br^- + 1)^{0.10} \cdot (Cl_0)^{-0.75} \quad (12-50)$$

The estimated regression model R^2 were 0.70 and 0.95, respectively. Equations were developed for chloroform, dichlorobromomethane, dibromochloromethane, bromoform, monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA), dibromoacetic acid (DBAA), tribromoacetic acid (TBAA), bromochloroacetic acid (BCAA), dibromochloroacetic acid (DBCBA), and dichlorobromoacetic acid (DCBAA).

Exposure to DBPs from Distribution Systems

Traditionally, EPA has established environmental regulatory programs for the protection of the outdoor environment from industrial and commercial sources of contamination. It has become increasingly clear, however, that indoor environments may pose a risk from contaminants that are found outside the household. For example, drinking water can be a carrier of contaminants that volatilize when they enter a household, thereby subjecting the consumer to inhalation, dermal, and ingestion exposure (Clark and Goodrich 1992). An EPA study found that personal or indoor exposures to many toxic or carcinogenic chemicals are greater than to outdoor concentrations. It also found that for all chemicals, except for THMs, the air provided greater than 99% of the exposure. Water provided nearly all of the exposure to the THMs and more than half of most exposure to chloroform.

Clark et al. (1992) demonstrated that the dynamics of multiple source mixing and system operation in a water distribution system can affect lifetime exposures to volatile organic chemicals such as chloroform. The dose received will depend on one's location within the system and the timing of water use. It was found that dynamic water quality models are valuable tools for conducting drinking water exposure assessments. They help in interpreting the results from field monitoring sites so that a clearer picture of the impact of distributed water emerges. They also provide time-varying estimates of drinking water quality at all locations within a service area so that more accurate exposure assessments can be made. A case study showed that for adults, the inhalation pathway for chloroform contributes more to total exposure than does the ingestion pathway at most locations within the service area, although the opposite is true for infants. Showering is the greatest potential contributor to household inhalation exposure. This analysis raised the question of equity in providing safe drinking water (Clark et al. 1992).

Modeling Chlorine Decay and TTHMs in Distribution Systems

EPA has conducted extensive research related to the application of models to chlorine decay and TTHM formation in drinking water distribution systems. This research has been a major contributor to an understanding of the factors that influence water quality in drinking water distribution systems and is discussed in this section.

North Penn Study

One of the first projects to investigate the feasibility of modeling water quality in drinking water distribution systems was conducted under a cooperative agreement initiated between the North Penn Water Authority (NPWA) in Lansdale, PA, and EPA. The project focused on the mixing of water from multiple sources and investigated the feasibility for development and application of a steady-state water-quality model. As the study progressed, it became obvious that the dynamic nature of both patterns of demand and variations in water quality required the development of a dynamic model. Techniques for semicontinuous monitoring of volatile organic contaminants were also explored (Clark et al. 1988b). At the time of the NPWA/EPA study, the authority served 14,500 customers in 10 municipalities and supplied an average of 19,000 m³/day (5mgd) (Clark et al. 1988b). The NPWA distribution system was modeled in a network representation consisting of 528 links and 456 nodes, and water demands for modeling represented conditions from May to July 1984. The network hydraulic model used was developed by the U.S. Army Corps of Engineers and contained provisions for both steady-state and quasi-dynamic hydraulic modeling for extended-period simulation (Gessler and Walski 1985).

The model revealed that significant portions of the system were subject to flow reversals. The velocity for each link was known from the hydraulic solution for each time period, which was evenly divided into an integer number of computational time steps. Each link was then divided into sublinks by a series of evenly spaced subnodes (though the distance between subnodes varied from link to link or for a link at different time periods), so that the travel time from a subnode (or node) to the adjacent subnode (or node) was approximately equal to a specified time step. A model called the Dynamic Water Quality Model (DWQM) was developed. The solution algorithm used in the DWQM operated sequentially by time period. During a time period, all external forces affecting water quality were assumed to remain constant (e.g., demand, well pumpage, tank head). The DWQM was used to simulate a 34-hour period corresponding to conditions present during the pilot-level sampling program conducted on November 14 to 15, 1985. Parameters of the model were adjusted so that predicted tank levels and flows at selected sites represented those measured during the sampling period. For chloroform, THM, and hardness, the predicted concentrations compared favorably with the observed values at the sampling stations.

South Central Connecticut Study

The North Penn case study provided an excellent test-bed for development of a dynamic water-quality model (Clark and Coyle 1990). To extend the North Penn application, EPA initiated another cooperative agreement with the University of Michigan and the South Central Connecticut Regional Water Authority (SCCRWA). The purpose of the cooperative agreement was to test the previously developed modeling concepts and to verify and calibrate the model through field investigations (Clark and Goodrich 1993; Clark et al. 1988a). At the time of the study, SCCRWA supplied water to approximately 95,000 customers (380,000 individuals) in 12 municipalities in the Greater New Haven area. The service area was divided into 16 separate pressure/distribution zones. Average production was 190,000 m³/day (50 mgd) with a safe yield of approximately 281,200 m³/day (74 mgd). Water sources included four surface water sources (Lake Gaillard, Lake Saltonstall, Lake Whitney, and the West River System) and five well fields (North Cheshire, South Cheshire, Mt. Carmel, North Sleeping Giant, and South Sleeping Giant). Approximately 80 percent of the water in use in the system came from surface sources; the remaining 20 percent came from wells. All surface water was treated with chlorination, filtration, and addition of a phosphate-corrosion inhibitor. The system included 22 pumping stations, 23 storage tanks, and approximately 2,091,700 m (1300 miles) of water mains. Preliminary efforts to develop and validate a model for the South Central System were concentrated on the Cheshire service area (Clark 1993b; Clark et al. 1993b).

This area was relatively isolated and provided a prototype for modeling the remainder of the system. To validate the model, an extensive study was planned in which the fluoride feed at the North Well Field was turned off and the propagation of the fluoride feed water was tracked through the system (Clark et al. 1991). Prior to the water-quality modeling effort and the related field study, extensive hydraulic analyses were conducted on the system. For the preliminary modeling effort, the full SCCRWA system network was represented by approximately 520 nodes and 700 links. In most cases, the network was represented by “skeletonizing” the system (i.e., selectively choosing pipes based on their size and perceived impact as transmission mains). The DWQM developed in the North Penn study was applied to the Cheshire system to simulate the propagation of fluoride feed water and also to select sampling locations for a field study. Based on the simulation results and the objectives of the proposed field study, a sampling scheme was designed. Fluoride was selected as the tracer because it was added regularly to the water at a concentration of approximately 1 mg/L, as required by the State Department of Health Services. Tracing the changes in the fluoride concentration in the distribution system allowed accurate travel times to be determined. The time the fluoride feed was shut down at the well fields was compared to the time it dissipated at the sampling points (Skov et al. 1991). The model predictions and the sampling results were extremely close.

The behavior of the storage tanks was of special interest. During the early portion of the sampling period, variations in tank levels were held to a minimum (less than 0.91 m [3 ft]). After 2 days, little change in fluoride concentrations was found in the tank and, as a result, the water level was then allowed to vary approximately 2.8 m (8 ft). The wider range in tank levels had the effect of turning the water over relatively rapidly. Even with the rapid turnover, it took nearly 10 days to completely replace old water with new water in the tanks. It was clear from this analysis that storage tanks could have a detrimental effect on water quality, particularly as water aged in the tank.

On August 13 to 15, 1991, another sampling program at the Cherry Hill/Brushy Plains Service Area was initiated with the goal of validating the previously discussed simulation results. The purpose of this sampling program was to gather information to characterize the variation of water quality in the service area and to study the impact of tank operation on water quality. The Cherry Hill/Brushy Plains Service Area covered approximately $5.18 \times 10^6 \text{ m}^2$ (2 mi²) in the Town of Branford in the eastern portion of the SCCRWA (Clark et al. 1993b). This service area was almost entirely residential, containing both single-family homes and apartment/condominium units. Average water use during the sampling period was 1700 m³ per day (0.46 mgd).

The water distribution system was composed of 20.3-cm (8-in) and 30.48-cm (12-in) mains. The terrain in the Cherry Hill/Brushy Plains Service Area was generally moderately sloping, with elevations varying from approximately 15.2 m (50 ft) mean sea level (MSL) to 70.1 m (230 ft) MSL. Cherry Hill/Brushy Plains received its water from the Saltonstall system. Water was pumped from the Saltonstall system into Brushy Plains by the Cherry Hill Pump Station. Within the service area, storage was provided by the Brushy Plains tank. The pump station contained two 10.2-cm (4-in) centrifugal pumps with a total capacity of 5300 m³/day (1.4 mgd). The operation of the pumps was controlled by water elevation in the tank. Built in 1957, the tank had a capacity of 3800 m³ per day (1.0 mgd). It had a diameter of 15.2 m (50 ft), a bottom elevation of 58.8 m (193 ft) MSL, and a height (to the overflow) of 80.2 m (263 ft) MSL. During normal operation, the pumps were set to go on when the water level in the tank dropped to 15.2 m (56 ft) and to turn off when the water level reached 19.8 m (65 ft). As had occurred during the study of the Cheshire service area, the hydraulic model developed by Gessler and Wolski (1985) and the DWQM were applied to establish flow patterns within the service area. In addition, during the periods of May 21 to 22, July 1 to 3, July 8 to 10, and July 30 to August 1, 1991, chlorine residuals were monitored at the tank and operational patterns (pump records), and variations in tank water level were studied.

On the basis of these model runs and field data, a sampling strategy was adopted that involved turning the fluoride off at the Saltonstall Treatment Facility and sampling for both fluoride and chlorine in the Cherry Hill/Brushy Plains Service Area. The intention was to use defluoridated water as a conservative tracer for the movement of flow through the system and for calibration the DWQM. The DWQM and a chlorine decay model based on hydrodynamic principles were used to model the dynamics of chlorine decay in the system. Seven sampling sites in the distribution system, in addition to sampling sites at the pump station and tank, were identified. A hydraulic model and the DWQM model were used to simulate the Cherry Hill/Brushy Plains Service Area for a 53-hour period from 9:00 am on August 13 to 3:00 pm on August 15, 1991. A skeletonization was developed representing the Cherry Hill/Brushy Plains distribution system, which included all 30.4-cm (12-in) mains, major 20.3-cm (8-in) mains and loops, and pipes that connected to the sampling sites. Pipe lengths were scaled from a map, actual pipe diameters were used, and, in the absence of any other information, a Hazen-Williams roughness coefficient of 100 was assumed for all pipes. From these results, it is clear that the modeling effort matched the sampling efforts well, with the exception of dead-ends.

It was clear that the pump cycles influenced water quality heavily at several sampling points. For example, at node 11, during the pumps-on cycle, the fluoridated water was pumped into the system. When the system was being fed from the tank (pumps-off), the system was receiving water that had reached an equilibrium concentration of fluoride before the stoppage of the fluoride feeders. As mentioned previously, the two scenarios evaluated during the sampling study were with the pumps-on and pumps-off condition. Using the upstream and downstream chlorine concentration and the residence times in the link, the chlorine decay coefficient was calculated for each link. Chlorine demand was calculated according to a first-order assumption, which is defined as follows:

$$C = C_0 e^{-rt} \quad (12-51)$$

where C = the concentration at time t , C_0 = initial chlorine concentration, r = decay rate in day^{-1} , and t = time in day. A bench study was conducted in which chlorine demand for the raw water was calculated using Cherry Hill/Brushy Plains water, and the chlorine decay rate was calculated as 0.55 day^{-1} . This decay rate might be regarded as the bulk decay rate or the decay rate of chlorine in the treated water. The total system demand was found to be two to three times higher than the bulk decay rate alone. It was concluded that this additional demand was caused by pipe wall demand, biofilm, and tubercles.

Development of EPANET

As a follow-up to the development of the DWQM and as a follow-up to the North Penn and SCCRWA studies, Rossman (1994) and Rossman et al. (1994) developed a mass transfer-based model for predicting chlorine decay in drinking water distribution networks. The model considers first-order reactions of chlorine to occur both in the bulk flow and at the pipe wall. The overall rate of the wall reaction is a function of the rate of mass transfer of chlorine to the wall and is therefore dependent on pipe geometry and flow regime. As observed in the SCCRWA study, the model can thus explain field observations that show higher chlorine decay rates associated with smaller pipe sizes and higher flow velocities. It has been incorporated into a computer program called EPANET that can perform dynamic water-quality simulations on complex pipe networks. It represents a third generation of water-quality models developed by the WSWRD to improve our understanding of the movement and fate of constituents within water distribution systems.

Advances contained in EPANET include a coordinated approach to modeling both network hydraulics and water quality, consideration of both bulk flow and pipe wall reaction mechanisms, and a graphical

user interface to aid in visualizing network behavior. The model's bulk decay rate constant is determined independently in the laboratory. Its wall decay constant can be varied over a range of values that include both reaction rate-limiting and mass transfer rate-limiting values. EPANET is based on the extended-period simulation approach to solving hydraulic behavior of a network. It has proven to be a very effective research tool for modeling the movement and fate of drinking water constituents within distribution systems. EPANET calculates all flows in cubic feet per second (cfs) and has an option for accepting flow units in gallons per minute (gpm), mgd, or liters per second (l/s). The Hazen-Williams formula, the Darcy-Weisbach formula, and the Chezy Manning formula can be used to calculate the head loss in pipes. It also models pumps, valves, and minor loss. To model water quality within distribution systems, the concentration of a particular substance must be calculated as it moves through the system from various points of entry (e.g., treatment plants) and on to water users. This movement is based on three principles: (1) conservation of mass within differential lengths of pipe, (2) complete and instantaneous mixing of the water entering pipe junctions, and (3) appropriate kinetic expressions for the growth or decay of the substance as it flows through pipes and storage facilities.

The model has been validated using data from various field studies. Resulting predictions have been compared with observed chlorine measurements at eight field sites. Good agreement was achieved at locations where the hydraulic conditions were well characterized. Model predictions were less accurate at sites where the hydraulic calibration was less precise. These results underscore the need to obtain accurate hydraulic information before running a network water-quality model.

North Marin Study

It is clear that, as dissolved chlorine travels through the pipes in the network, it reacts with NOM in the bulk water and with biofilm and tubercles on the pipe walls or with the pipe wall material itself (Clark et al. 1993a). This reaction results in a decrease in chlorine residual and a corresponding increase in DBPs, depending on the residence time in the network pipes and holding time in storage facilities. Understanding these reactions will help water-utility managers deliver high-quality drinking water and meet regulatory requirements under the 1996 SDWA and amendments. Water-quality modeling has the potential to provide insight into the factors that influence the variables affecting changes in water quality in distribution systems. Understanding the factors that influence the formation of TTHMs and maintenance of chlorine residuals is of particular interest (Clark et al. 1995).

EPANET has proved to be especially useful for modeling both formation of TTHMs and the propagation and maintenance of chlorine residuals. Among the first studies to address these issues using EPANET was one conducted by EPA in collaboration with the North Marin Water District (NMWD) in California (Clark et al. 1994). Another recently completed study conducted jointly by EPA and the AWWARF examined these same issues (Vasconcelos et al. 1997). This study evaluated various types of models to describe both the formation of TTHMs and loss of chlorine residual and will be discussed later in this chapter.

At the time of the North Marin study, the district served a suburban population of 53,000 people who live in or near Novato, California. It used two sources of water: Stafford Lake and the North Marin Aqueduct. The aqueduct is a year-round source, but Stafford Lake is in use only during the warm summer months, when precipitation is virtually nonexistent and demand is high. Novato, the largest population center in the North Marin service area, is located in a warm, inland coastal valley with a mean annual rainfall of 68.6 cm (27 in). Virtually no precipitation occurs during the growing season from May through September. Eighty-five percent of total water use is residential, and the service area contains 13,200 single-family detached homes, which accounted for 65 percent of all water use (Clark et al. 1994). The water quality of the two sources differs greatly. Stafford Lake water had a high humic content and was treated with conventional treatment and prechlorination doses of between 5.5 and

6.0 mg/L. The treated water had a residual of 0.5 mg/L when it left the treatment plant clearwell. The potential for formation of THMs in the Stafford Lake water was high. The North Marin Aqueduct water was derived from a Raney Well Field along the Russian River. Technically classified as ground water, the source water contained a high proportion of naturally filtered water. Aqueduct water was disinfected only and was low in precursor material, with a correspondingly low potential for formation of THMs. Both sources carried a residual chlorine level of approximately 0.5 mg/L when the water entered the system.

The major focus of the study was Zone 1 of the NMWD distribution system. Depending on the time of year and the time of day, water entered the system from either one source or both sources. The North Marin Aqueduct source operated year-round, 24 hours per day. The Stafford Lake source operated only during the peak demand period from 6:00 am to 10:00 pm and generally operated for 16 hours per day. EPANET was used to model the system hydraulics, including the relative flow from each source, TTHMs, and propagation of chlorine residual (Rossman et al. 1994). The model was based on an earlier representation of the network made by Montgomery Watson, Inc., for North Marin and was calibrated based on a comparison of simulated versus actual tank levels for the May 27–29, 1992, period of operation. The dynamic nature of the system led to variable flow conditions and variable water quality in the network. Flow directions frequently reverse within a given portion of the network during a typical operating day. The consequences of these variable flow patterns for water quality are significant.

To characterize the water quality in the NMWD, EPA designed a sampling protocol and sent a team of investigators to work with the district staff for the period May 27–29, 1992. The water quality is highly variable. For example, at the Eighth Street sampling point, chloroform levels varied from 38.4 to 120.1 $\mu\text{g/L}$ over the 2-day period. This variability was caused by the penetration of water from the two different sources. A regression relationship between UV absorbance and THMs was established using the data from both sources. The assumptions of the model (constant variance and normality of error terms) were checked and deemed to be reasonable. Both Stafford Lake water and the North Marin Aqueduct water generally maintained a chlorine residual level of 0.5 mg/L as the treated water entered the system. As mentioned, the Stafford Lake water had a much higher chlorine demand than did the Aqueduct water.

To predict chlorine demand at the various sampling points, a first-order decay relationship was assumed (Clark et al. 1995). In EPANET, chlorine decay is represented by decay in the bulk phase and by decay in the pipe wall. Based on bulk water calculations, the first-order decay coefficients or bulk demand for the Stafford Lake and the Aqueduct sources were 0.31 and 0.03 day^{-1} , respectively. Using EPANET and the previously assumed hydraulic conditions, the chlorine residuals were estimated. It was evident from the analysis that the pipes in the distribution network exhibited a demand for chlorine. This demand probably comes from tubercles, biofilm, and perhaps the pipe wall material itself (Clark et al. 1995). A comparison between chlorine residuals using the first-order assumptions predicted from EPANET versus actual chlorine residuals provided an excellent illustration of this point. It became clear that the demand in the system went beyond just bulk-water decay. Because EPANET has the capacity to incorporate a wall demand factor in addition to the bulk demand factors for chlorine, the system was simulated again using the bulk demand for the two sources, and trial and error was used to estimate wall demands for four sections of the network. When chlorine residuals were re-estimated at the four sampling points, wall demand obviously played a major role in chlorine residual loss. This pipe wall demand may be the result of the source or the age of the system. For example, the maximum wall demand was found in the areas served primarily by Stafford Lake. However, those pipes were also the oldest in the system.

EPA/AWARF Study

Vasconcelos et al. (1997), in a study sponsored jointly by EPA and AWWARF, investigated the factors leading to loss of chlorine residuals in drinking water distribution systems. Kinetic rate equations were

developed, tested and evaluated based on data collected from five drinking water utilities. This investigation uncovered a number of findings concerning the mechanisms of chlorine decay and the kinetic models that describe it. The most significant findings of this study included the following:

- Chlorine decay in distribution systems can occur because of reactions within the bulk fluid and with the pipe wall demand.
- The rate of reaction of chlorine at the pipe wall is inversely related to pipe diameter and is mass transfer limited.
- There is no established method for directly determining the kinetics of chlorine decay attributable to pipe wall reactions. These values must be determined from field data.
- A well-calibrated hydraulic model is a prerequisite for attempting to model water quality in a distribution system.
- Calibration of network chlorine decay models can be based on first-order kinetic models for bulk reactions and either first-order or zero-order kinetics for wall reactions.
- The wall kinetic constant appears to be inversely related to the pipe roughness coefficient.
- A non-reacting chemical should be used when calibrating a model during field studies.

Based on the experience gained during this study, the following recommendations for future work are offered:

- More direct methods of estimating pipe wall-related chlorine reaction constants are needed.
- Sensors in the distribution system coupled with remote telemetry may offer a way to perform continuous on-line calibration of network chlorine decay models.
- Water quality models should be enhanced to better accommodate different water sources when each source water exhibits different bulk reaction kinetics.
- As an increasing number of systems calibrate chlorine decay models, it may be possible to establish a database relating kinetic parameters to water chemistry and pipe characteristics.

Evolution of System Modeling

On the basis of the results from the case studies previously described and from other studies reported in the literature, it is obvious that water-quality modeling has the potential to provide insight into the factors that degrade water quality in networks. It has also become increasingly obvious that, despite the treatment investments being forced by regulations in the 1996 SDWA and amendments, the potential exists for deterioration of water quality in the network itself. This realization led to the development of several public- and private-sector water-quality models. Only the public-sector models will be discussed here. EPANET, developed by Rossman (1994) and Rossman et al. (1994), as discussed earlier, was based on mass transfer concepts.

Another approach to the propagation of contaminants was developed by Biswas et al. (1993) using a steady-state transport equation. It accounted for the simultaneous advective transport of chlorine in the axial direction, diffusion in the radial direction, and consumption by first-order reaction in the bulk-liquid phase. Islam (1995) and Islam et al. (1997) developed a model called QUALNET, which predicted the temporal and spatial distribution of chlorine in a pipe network under slowly varying unsteady-flow conditions. Boulos et al. (1995) proposed a technique called the Event-Driven Method (EDM), which is based on a next-event scheduling approach and can significantly reduce computing times.

Several different types of numerical methods have been proposed to solve these types of models, including the Eulerian Finite-Difference Method (FDM), the Eulerian Discrete-Volume Method (DVM), the Lagrangian Time-Driven Method (TDM), and the Lagrangian Event-Driven Method (Rossman and Boulos 1996). The FDM approximates derivatives with finite-difference equivalents along a fixed grid

of points in time and space. Islam et al. (1997) used this technique. The DVM divides each pipe into a series of equal-sized, completely mixed volume segments. At the end of each successive water-quality time step, the concentration within each volume segment is first reacted and then transferred to the adjacent downstream segment. This approach was used in the models that were the basis for the early DWQM studies. The TDM tracks the concentration and size of a non-overlapping segment of water that fills each link of a network. As time progresses, the size of the most upstream segment in a link increases as water enters the link, whereas an equal loss in size of the most downstream segment occurs as water leaves the link. The size of these segments remains unchanged. The EDM is similar in nature to the TDM, but rather than update an entire network at fixed time steps, individual link/node conditions are updated only when the leading segment in a link disappears completely through this downstream node. The development of the EPANET hydraulic model has satisfied the need for a comprehensive public-sector model and has been a key component in providing the basis for water-quality modeling in many utilities throughout the U.S.

Advances in Numerical Modeling Techniques

In addition to the development and application of EPANET, other “spin-off” research has resulted in models that locate monitoring stations in networks, predict the propagation of disinfectants, and determine the location of booster chlorination. This research is summarized in the following text.

Lee et al. (1991) examined the problem of selecting monitoring stations that will adequately monitor the changes in water quality between the time water leaves the treatment plant and the time it reaches the customer’s tap. They found that there is no uniform schedule or framework for monitoring under the SDWA. This lack of specificity poses both management and technical barriers to states and water systems ultimately responsible for implementation of the regulations. The authors provided systematic and quantitative guidelines for locating monitoring stations. Their guidelines are based on the concept of pathways. The authors applied the concept of coverage and inferred the quality at an upstream node from the quality at a downstream node.

Lu et al. (1993, 1995) developed mathematical models to predict disinfectant concentration profiles under breakpoint chlorination conditions and to predict the growth of biofilm in drinking water distribution systems. The breakpoint chlorination model accounts for concurrent mass transfer and a series of chemical reactions under breakpoint chlorination conditions, and the other is developed to predict disinfectant concentration profiles in the drinking water distribution pipe. The disinfection model is validated by comparing its numerical solutions to experimental data in the literature. The impact of important parameters on the model performance is examined by sensitivity analysis. Practical applications of the model to minimize water-quality deterioration in the distribution system are discussed. It is intended to provide insight into the factors that influence all of the fundamental reactions and disinfectant transport of the breakpoint reaction. Operational criteria for the chlorination of distributed water are derived.

Rossman and Boulos (1996) compared the formulation and computational performance of four numerical methods for modeling the transient behavior of water quality in drinking water distribution systems. Two are Eulerian-based (the finite-difference and discrete-volume methods) and two are Lagrangian-based (the time-driven and event-driven methods). In the Eulerian approaches, water moves between fixed grid points or volume segments in pipes as time is advanced in uniform increments. The Lagrangian methods update conditions in variable-sized segments of water at either uniform time increments or only at times when a new segment reaches a downstream pipe junction. Each method was encoded into an existing distribution system simulation model and run on several pipe networks of varying size under equal accuracy tolerances. Results show that the accuracies of the methods are comparable. The Lagrangian methods are more efficient for simulating chemical transport. For model-

ing water age, the time-driven Lagrangian method is the most efficient, while the Eulerian methods are more memory-efficient. Results of the study showed the following: the numerical accuracy of the methods was by and large the same, with the exception that FDM occasionally smeared sharp concentration fronts and DVM occasionally accelerated the arrival of concentration changes. All of the methods were capable of adequately representing observed water-quality behavior in actual water distribution systems. Regardless of the method used, network size was not always a good predictor of the solution time and amount of memory required.

Boccelli et al. (1998) studied disinfectants added at discrete locations in a water distribution system. Such a strategy can reduce the mass of disinfectant required to maintain a detectable residual at points of consumption in the distribution system, which may lead to reduced formation of DBPs, in particular THMs. An optimization model is formulated for the dynamic schedule of disinfectant injections, which minimizes the total dose required to satisfy residual constraints over an infinite-time horizon. This infinite-time problem is reduced to a solvable finite-time optimal scheduling model by assuming periodicity of mass injections and network hydraulics. Furthermore, this principle of linear superposition is shown to apply to disinfectant concentrations resulting from multiple disinfectant injections over time. A matrix generator code was developed to interface with the EPANET network water-quality model. This code automatically generates the linear programming formulation of the optimal scheduling model, which is then solved using the simplex algorithm. Results from application of the model suggest that booster disinfection can reduce the amount of disinfectant required to satisfy concentration constraints when compared to conventional disinfection practiced only at the source. The optimal booster schedule reduced the average disinfectant concentration within the distribution system and, in some cases, the variability of these concentrations. The number of booster stations, booster location, and distribution system hydraulics were shown to affect the optimal schedule.

Lu et al. (1995) developed a biofilm model that accounts for simultaneous transport of substrates, disinfectants, and microorganisms and that predicts substantial changes in quality of distributed water. The model consists of a set of mass balance equations for organic substances, ammonia nitrogen, oxidized nitrogen, dissolved oxygen, alkalinity, biomass, and disinfectants in the bulk liquid phase and within the biofilm under laminar and turbulent flow conditions. This model is validated by comparing its solutions with numerical solutions in the literature and is then applied to predict the behavior of a typical water treatment plant effluent through a distribution pipe. The flow properties and disinfectant consumption rate at the pipe wall play a significant role in the determination of potable water quality in the distribution system.

Tryby et al. (1999) examined the feasibility of using booster chlorination in distribution systems. They developed a conceptual model for bulk chlorine decay under booster conditions. The conceptual analysis demonstrated that the use of booster chlorination allows microbial inactivation and maintenance of a detectable residual to be viewed as separate treatment issues. Booster chlorination could allow dosages to be reduced at the water treatment plant without compromising treatment objectives. By reducing dosages, the DBP yields at the water treatment plant may also be reduced and the disinfectant mass conserved can be more efficiently applied at points located in the distribution system. Their studies suggest that increasing residual concentrations alone will not eliminate the risks associated with pathogens and biofilm regrowth in problem areas. Several barriers against the entrance of contaminants are required. However, booster disinfection is the most efficient method of minimizing DBP formation.

Water Quality and Tanks

The issue of water quality as affected by storage tank design and operation has been the object of extensive study. Most of this research has been conducted by EPA and AAWARF. The major studies in this area are presented in the following paragraphs.

Grayman and Clark (1993) conducted a series of studies demonstrating that water quality is degraded as a result of long residence times in storage tanks, which in turn has highlighted the importance of tank design, location, and operation. Computer models were developed to explain the effect of tank design and operation on various water-quality parameters. The diversity of the effects and the wide range of design and environmental conditions make general design specifications for tanks unlikely. The authors recommend that modeling be refined to facilitate site-specific analysis.

Mau et al. (1995) developed explicit analytical mathematical models for use in water-quality simulation studies and management of distribution system storage. The proposed models can be used for investigating the mixing characteristics of tanks and their subsequent effects on water quality. They can directly supplement any of the existing distribution system water-quality simulators. These models are formulated analytically from mass balance principles and based on hydrodynamic processes. The resulting models are simple to understand and implement and are well suited to the needs of practicing engineers. The performance models are validated by application to actual tank data.

Rossman et al. (1995) studied the factors leading to the loss of disinfectant residual in well-mixed drinking water storage tanks. Equations relating disinfectant residual to the disinfectant's reaction rate, the tank volume, and the fill and drain rates were developed. The authors presented an analytical solution for the minimum disinfectant residual in the tank under constant inflow/outflow conditions. It showed that significant disinfectant loss begins when the product of disinfectant decay constant and the refill time for an empty tank exceeds 0.1 and that disinfectant residuals are relatively insensitive to the fraction of total volume devoted to emergency storage. A second, numerical solution to the model is developed to account for the fact that tank fill and drain rates are constrained by system demand patterns, pump capacity, and pump scheduling. Results from their study showed that pulsed or periodic pumping during a portion of the day can maintain much higher disinfectant residuals than continuous pumping can.

Clark et al. (1996a) demonstrated the use of compartment models to characterize mixing in three tanks. It was found that the mixing regimes in these tanks were well characterized by compartment-type models and that these tanks were not completely mixed, contrary to conventional wisdom. For purposes of this analysis, one-, two-, or three-compartment models were developed. It is clear that, in some cases, compartment models provide a very good representation of the mixing and residence times in tanks. It is also clear that additional research needs to be conducted in this area.

Boulos et al. (1996) conducted an extensive study of reservoir water quality at the Ed Heck reservoir in Azusa, CA. Emphasis was placed on understanding the hydraulic mixing regime and the distribution of the free chlorine residuals in the reservoir. A unique roof-mounted sampling device was developed for the study that allowed samples to be extracted from various depths in the water column. The device proved to be very effective and greatly enhanced the study's findings. The following conclusions were drawn:

- Fluoride tracer studies are useful for determining residence time distributions and internal mixing dynamics
- In the Ed Heck reservoir, the flow pattern was a relatively fast rotational flow around a large outer annular ring coupled with a slower downward flow within a smaller central core.
- For the conditions governing this study, the reservoir behaves, on average, as a completely mixed reactor.
- The mean residence time of 9.7 hours and a negligible loss of free chlorine residual was experienced during the course of the study.
- Short-circuiting between the inlet and outlet lines caused the T_{10} for the reservoir to be less than half that of a true continuous-flow stirred-tank reactor (CSTR).

Boulos et al. (1998) developed and verified an explicit mathematical model of distribution storage water quality based on a compartmental representation of the reservoir continuum. It was formulated analytically based on mass balance relationships which are applicable to separate inlet and outlet configuration reservoirs with simultaneous dual-directional flow. Previous models considered a common inlet/outlet reservoir configuration with unidirectional flow. The model was verified by application to actual reservoir data taken from a storage reservoir in Azusa, CA. Both conservative (fluoride) and reactive (chlorine) species were considered. A four-compartment model resulted in a reasonable fit between observed and simulated concentrations and should be predictive under operating conditions similar to those under which the model was calibrated.

Rossman and Grayman (1999) reported on experiments conducted on cylindrical scale-model tanks designed to determine the effect of various factors on mixing in the tanks. It was found that the time required to mix the contents of a tank with water introduced during the fill period was proportional to the initial volume to the two-thirds power divided by the square root of the inflow momentum flux (the product of flow rate and velocity). The time is insensitive to the orientation of the inlet (vertically or horizontally). Complete mixing depends on the ratio of the momentum to buoyancy fluxes of the inlet jet. This is similar to past findings for jet discharges to unconfined bodies of water. The confined geometry of the tank results in a narrower range of conditions that produce stratification. The investigators derive a formula to estimate the minimum volume exchange required for a fill-and-draw cycle to ensure complete mixing before the end of the filling period.

Policy Issues

There are many policy implications to the research discussed in this chapter. Two papers (Clark et al. 1994, 1995) attempted to frame some of the issues that modeling results have raised with respect to water quality in drinking water distribution systems.

Clark et al. (1995) discuss the SDWA and its amendments, which has focused interest on the factors that cause the deterioration of water between the treatment plant and the consumer. The authors discuss how the distribution system itself can contribute to this deterioration. Numerous examples of water-borne outbreaks have demonstrated the importance of the distribution system in preventing disease. The authors discuss water-quality propagation models that can be used to study the factors that contribute to water-quality deterioration. These models have been used in many locations to study contaminant propagation. This paper describes the application of contaminant propagation models in the SCCRWA. In this study, the fluoride feed was cut off at the water treatment plant to calibrate the model and determine residence times in the system. An extensive simulation of the system was conducted to predict conservative contaminant propagation and chlorine decay. After completing the simulation study, a sampling program was conducted to verify the results from the model. In general, the field results verified the model predictions. Water quality varied widely over the service area. Long retention times in storage tanks and pipe wall demand, especially in dead-end sections, caused significant losses in chlorine residuals.

Clark et al. (1994) present models that might be used to evaluate the consequences of investing in treatment and/or investing in replacement, rehabilitation, or repair of the pipe network to improve water quality. The authors point out that water high in humic and organic material that is transported in the network can ultimately lead to pipes that have a high disinfectant demand. Investment in treatment might not only meet water quality; it might also lead to a “cleaner” network.

Summary and Conclusions

Conventional treatment combined with disinfection has proven to be one of the major public health advances of modern times. In the U.S., chlorine has been the final disinfectant most often used before

drinking water is discharged into a drinking water distribution system. It is added to provide a residual and to protect against microbial contamination. However, disinfectants, especially chlorine, react with NOM to form DBPs, which are considered to be of concern from a chronic exposure point of view. Disinfection reduces risk of infectious disease, but the interaction between disinfectants and precursor materials in source water result in the formation of DBPs.

Even treated drinking water exerts chlorine demand due to the reactions with NOM and other constituents in water. Therefore, the disinfectant dose must be sufficient to meet the inherent demand in the treated water, to provide sufficient protection against microbial infection, and at the same time minimize exposure to DBPs.

The factors that cause the disappearance of residuals and the subsequent formation of DBPs has been the subject of extensive study. Much of this effort has been devoted to models which are intended to identify the factors that influence both residual decay and the formation of DBPs. This chapter has reviewed both the EPA-supported research in this area as well as research conducted outside the Agency. Clearly, much progress has been made in developing realistic models to support risk management goals. Of particular note is the application of models to field conditions in water utilities. There is, however, much research left to be done before these models are truly predictive.

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